

Insights into Microscopic Diffusion Processes at a Solid/Fluid Interface under Supercritical Conditions: A Study of the Aqueous Calcite ($10\bar{1}4$) Surface

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We use molecular dynamics (MD) and non-Markovian kinetic Monte Carlo (KMC) simulations to investigate diffusion processes at an aqueous calcite ($10\bar{1}4$) interface under various geologically relevant supercritical conditions. We show that solvent properties can change dramatically as a function of temperature and pressure and that complex interactions among the adsorbents, surface, and solvent molecules control the dynamics at the interface. Despite its apparent simplicity, this interface exhibits a non-trivial dynamical behavior. Our work proposes a new strategy to study fundamental issues related to solid-liquid interfaces at high temperatures and pressures.

Phenomena occurring at mineral interfaces in supercritical fluids are of fundamental importance in a wide range of Earth systems, including formation of ore deposits, ocean-floor hydrothermal systems, metamorphism within the continental lithosphere, geologic carbon sequestration, and geothermal energy production. Computer simulations are a promising tool for the study of such systems, especially considering the difficulty of carrying out experiments in such extreme conditions.

For example, the diffusion of adsorbed particles at a solid/fluid interface is a phenomenon of great fundamental interest and technological importance. It is known that adsorbed particles at a solid surface can undergo two types of surface translational motion—*in-surface self-diffusion* and *bulk-mediated surface diffusion* (BMSD) [1]. BMSD occurs when a fluid is present above the solid surface. An adsorbed particle can then desorb from the surface and re-adsorb elsewhere, leading to effective surface displacements. Since bulk diffusion is much faster than in-surface diffusion, lateral diffusion can be enhanced when bulk diffusion is involved.

In this work, the aqueous calcite ($10\bar{1}4$) surface was chosen as a model system to study diffusion at solid/fluid interfaces. We use MD and KMC to simulate diffusion processes under various geologically relevant supercritical conditions (101.3 MPa, 300-800 K). A force field developed by Raiteri et al. [2] is used to simulate the interactions in the aqueous calcite system.

The free energy profiles of a calcium carbonate (CaCO_3) molecule desorbed from the calcite ($10\bar{1}4$) surface were first computed for $T=300$ -800 K at 101.3 MPa. The results are summarized in Fig.1(a). Here the reaction coordinate is the vertical distance between the adsorbent carbon atom and the calcite surface. As T increases from

300 to 800 K, the bulk water density [Fig.1(b)] decreases from 1.030 to 0.477 g/cm³. The relative heights of the second and the third density peaks also decrease with T , indicating a decrease in ordering of the water at the interface. As a result, dissolution of CaCO_3 becomes less favorable and the equilibrium position (corresponding to the free energy minimum) moves closer to the surface as T increases (Fig. 2).

One important consequence of the changes in the free energy profile is to modify the dependence of the desorption rate on T . Figure 1(c) shows that the ratio of the desorption free-energy barrier ΔG_d to the thermal energy $k_B T$ decreases from 300 to 600 K, so that in this region the tendency for desorption increases with T as we would expect. However, the trend reverses at 600 K, reflecting the sudden increase of the desorption free-energy barrier. This unusual desorption trend makes this an excellent model system for studying various diffusive regimes of BMSD.

We utilized a non-Markovian KMC algorithm with a set of predefined states (the set of free energy minima) and their corresponding first-passage time distributions to generate long state-to-state trajectories of CaCO_3 monomer diffusion at the surface. The diffusion processes in the perpendicular (to the surface) and lateral directions are treated independently. Perpendicular diffusion is modeled by the Smoluchowski equation while the lateral diffusion is treated as free 2D Brownian motion with an effective diffusivity appropriate for that state.

The values of the mean lateral diffusivity, D , estimated from the long-time limit of the mean squared displacement (MSD) for various T and contact water thicknesses are summarized in Fig. 3(a). As seen in the figure, D increases with contact water thickness due to increasingly significant contributions from bulk diffusion. D also increases with T and reaches its maximum value at 600 K. For $T > 600$ K, the system switches to inner-sphere type adsorption [Fig. 2(b)] and D consequently decreases.

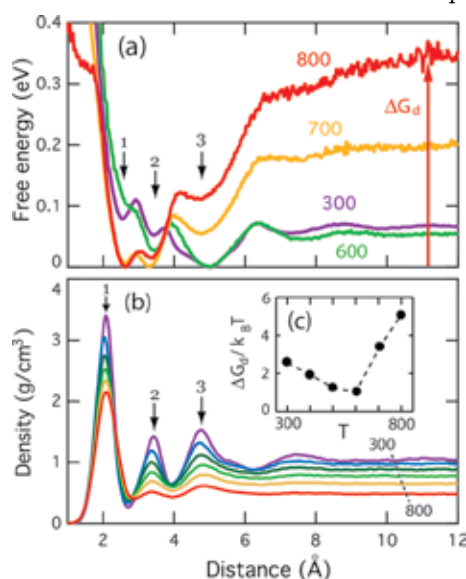


Fig 1. (a) Free energy of a CaCO_3 molecule desorbed from the aqueous calcite ($10\bar{1}4$) surface at various T and 101.3 MPa. (b) Mass density of water oxygen as a function of vertical distance. All densities were transformed to the corresponding water density. (c) The ratio $\Delta G_d/k_B T$ as a function of T .

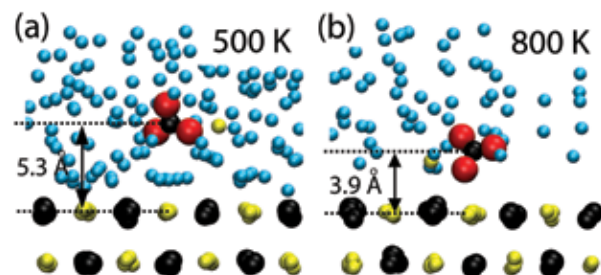


Fig. 2. Snapshots of MD simulations at 101.3 MPa at temperatures of (a) 500 K and (b) 800 K.

In order to validate the continuum model, we compare with direct MD simulations for a thickness of 12 Å [note black dots in Fig. 3(a)]. The agreement is very good, demonstrating that our model captures the essential factors controlling the diffusion process.

It is known that BMSD exhibits non-Fickian diffusion behaviors with anomalous scaling properties [1]. The short-time scaling of the diffusion process reveals more detailed information about the desorption kinetics. For an aqueous calcite system with infinite contact water, the short-time (~1 ns) effective MSD at various T s is summarized in Fig. 4.

By comparing the MSD trends with the in-surface diffusion lines (black), it is clear that the MSD curves at 300, 700, and 800 K exhibit a super-diffusive trend (i.e., they are concave and diffuse faster than in-surface diffusion) while others are sub-diffusive (i.e., they are convex and diffuse slower than in-surface diffusion).

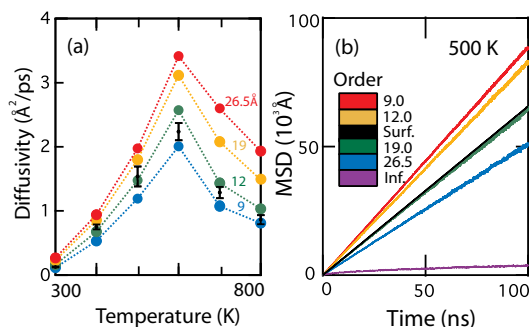


Fig. 3. (a) Monomer diffusivities obtained from the MSD curves for various temperatures and water thicknesses. The black dots with error bars are results from direct MD simulations with a contact water thickness of 12 Å. (b) Effective MSD as a function of time for various water thicknesses at 500 K. The MSD line estimated from surface diffusivity is also included in the plots (black solid lines).

From Fig. 4 it is clear that the desorption/adsorption kinetics affect the scaling properties of the effective diffusion. It has been reported that diffusion trends can also be affected by the contact fluid thickness [3]. We investigated this effect by varying the contact water thickness in the calcite system. For a given T , 500 K for example, the effective surface diffusion can be faster or slower than the in-surface diffusion depending on the water thickness [Fig. 3(b)]. It is interesting to note that the optimized water thickness that maximizes the effective surface diffusivity also varies with T .

In conclusion, we studied how the diffusion dynamics at a calcite/water interface change under different supercritical conditions. The MD and KMC simulations showed the effective lateral diffusion at the interface is greatly affected by the water conditions. This is a clear example of the tunable solvation power of supercritical fluids and of their effect on the diffusion dynamics of absorbed species. We believe these factors will affect the efficiency of surface mass transport and must be understood to predict reaction kinetics and transport efficiencies (including the relative importance of surface diffusion versus diffusion in bulk fluids) in conditions relevant to crustal geologic and energy systems.

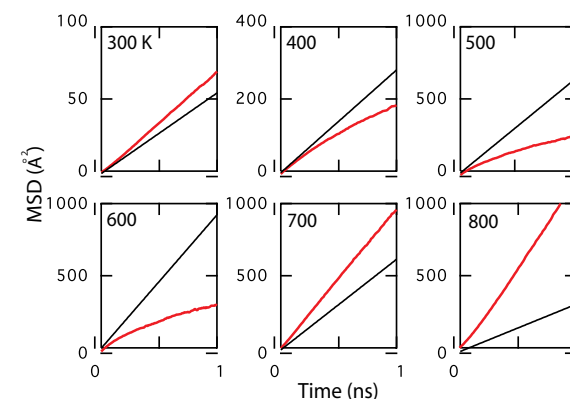


Fig. 4. Short-time effective MSD (red solid lines) as a function of time for various T . The calcite surface is in contact with infinite water. Black solid lines represent the same quantities for in-surface diffusion.

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